



Methanothermal reduction of mixtures of PbSO_4 and PbO_2 to synthesize ultrafine α - PbO powders for lead acid batteries

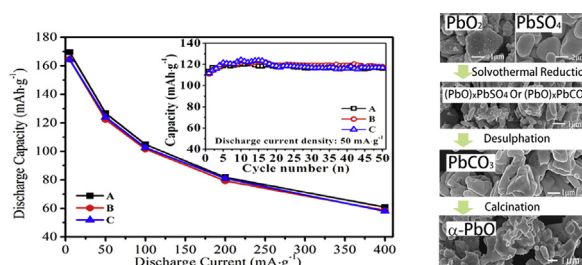
Pengran Gao, Yi Liu, Weixin Lv, Rui Zhang, Wei Liu, Xianfu Bu, Guanghua Li, Lixu Lei*

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China

HIGHLIGHTS

- PbO can be prepared by a solvothermal reaction of mixture of PbSO_4 and PbO_2 within methanol.
- The prepared PbO can discharge a capacity of 165 mAh g^{-1} at 5 mA g^{-1} .
- The prepared PbO from “the spent” discharge a capacity of 170 mAh g^{-1} at 5 mA g^{-1} .
- This paper shows a new way for the recycle of spent lead acid battery.

GRAPHICAL ABSTRACT



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ABSTRACT

Three artificial mixtures of PbSO_4 and PbO_2 as well as the active materials obtained directly from the positive plates of spent batteries have been solvothermally treated in methanol at 140°C for 24 h, which produce mainly $\text{PbO}\cdot\text{PbSO}_4$. The $\text{PbO}\cdot\text{PbSO}_4$ can be easily desulphated with ammonium carbonate to produce PbCO_3 , which can be calcined to form α - PbO to be used as positive active material of lead acid batteries. The α - PbO powders are irregular particles and highly electrochemically active, which discharges around 165 mAh g^{-1} at 5 mA g^{-1} , 80 mAh g^{-1} at 200 mA g^{-1} and 60 mAh g^{-1} at 400 mA g^{-1} with excellent cyclic stability in 50 cycles. SEM investigations show that the as-formed $\text{PbO}\cdot\text{PbSO}_4$ may inherit and enhance the morphological characteristics of PbSO_4 , and carbonation of $\text{PbO}\cdot\text{PbSO}_4$ does not destroy the rod-like characteristics. For the active material from the positive plates of spent lead acid batteries, the discharge capacities are 170 mAh g^{-1} at the current density of 5 mA g^{-1} , and 60 mAh g^{-1} at 400 mA g^{-1} , which is also similar. In 50 cycles, its capacity loss is only 5%.

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1. Introduction

Economic and social development demands growing energy supplies that traditional sources from fossil fuels cannot catch up; therefore, more and more researchers have focused on new energy sources [1–3], especially solar energy. Due to their instability, electric energies from photovoltaics, wind turbines and tidal streams have to be averaged by energy storage systems [4,5]. Those

energy storage systems have to be of high capacity and cost effective. Lead acid battery system is one of the such industrial products that meet the requirement, which changes electric power into chemical energy or vice versa [6,7]. Together with this, the other uses of lead acid batteries make them occupy a half share of battery market.

Wide utilisation of lead acid batteries of course generates a great deal of spent lead acid batteries. Those lead acid batteries currently have been recycled industrially through metallurgical processes, which are of high-energy consumption and very probable pollution; therefore, plenty of researches have been done to explore hydrometallurgical recycle process [8–11]. For example, it was

* Corresponding author.

E-mail address: lixu.lei@seu.edu.cn (L. Lei).

suggested that the spent lead paste was dissolved in HBF_4 or H_2SiF_6 to prepare $\text{Pb}(\text{BF}_4)_2$ or PbSiF_6 , which was then electrolyzed to recycle lead [12,13]. Although this method can definitely produce pure lead, the high-energy consumption in electrolysis and the usage of the toxic and corrosive chemicals make it difficult to be industrialized. Recently, Pan [14] demonstrated an interesting hydrometallurgical process to recover lead based on a hydrogen–lead oxide fuel cell. Through this process, lead of high purity, along with electricity, is produced with only water as the by-product.

A shortcoming for all those metallurgical processes is that the metallic lead cannot be used directly in lead acid batteries; it has to be oxidized again to produce leady oxide, and then be used. Because both the lead recovering and leady oxide making exhaust energy, we suggested processes for direct preparation of lead oxide from used batteries [15–17], in which the spent batteries are gently cut to separate the positive plates and negative plates. By such a means, it is possible to obtain the positive and negative active materials, respectively, which are then separately treated by chemical method to obtain PbO for positive and negative active materials [18,19]. At about the same time, Kumar and his colleagues [20–22] reported that the spent lead paste could be treated with an aqueous solution of citric acid to generate lead citrate, which can be calcined to produce a fine PbO powder. However, the authors did not report its electrochemical properties.

As we know, the active materials obtained from the positive plates of spent lead acid batteries contain lead sulphate and lead dioxide. Consequently, they have to be converted into electrochemically active PbO first. Earlier in 2013, our first paper on this issue [23] reported the preparation of PbO from commercial PbSO_4 , and the as-prepared PbO performs well electrochemically. Later, our second paper [18] reported that the lead dioxide, which is also a component of the spent positive material, can be converted into highly electrochemically active PbO through a solvothermal reduction in methanol. Those papers reported PbO prepared from pure raw materials, of course, we were interested in what will happen if they are mixed. Therefore, our third report was designed to reveal the behaviour of artificial mixtures of PbSO_4 and PbO_2 as well as the mixture from the spent positive plates active material. After carbonation, the mixtures are treated as that PbO_2 was treated to produce PbO [19]. It has been shown that the desulphation of the mixtures produces the mixtures of PbCO_3 and PbO_2 ; and the mixtures of PbCO_3 and PbO_2 can be reduced by methanol in a closed vessel at 140°C , and the products are PbO and $\text{PbO}\cdot\text{PbCO}_3$, which can be calcined to produce highly active $\alpha\text{-PbO}$. Interestingly, the activity is almost the same no matter what the composition of the mixture is: they discharge around 170 mAh g^{-1} at 5 mA g^{-1} with excellent cyclic stability in 50 cycles.

Although the results show that the composition of the mixtures of PbO_2 and PbSO_4 do not affect the electrochemical property of the PbO , it is unknown what role the PbCO_3 in the desulphated mixture plays during the methanothermal reduction of PbO_2 . It has been revealed that $\text{PbO}\cdot\text{PbCO}_3$ has been produced; we are wondering that what happens if the mixture is not desulphated, or if PbSO_4 behaves just like PbCO_3 ? In this paper, the mixtures are methanothermal reduced directly, and the as-obtained solid is then desulphated and calcined to produce PbO . In contrast to the previous procedure, the current method will be denoted as post-desulphation method.

2. Experimental

2.1. Material preparation

Three mechanical mixtures of lead sulphate (AR, 99.0%, Aladdin Chemical Reagent Co., Ltd.) and lead dioxide (AR, 98.0%, Aladdin

Chemical Reagent Co., Ltd.) in molar ratios of 2:1, 1:1 and 1:2 were prepared, respectively. In addition, the positive material was obtained from the positive plates of spent batteries.

The solvothermal treatment of each mixture was carried out as follows: 20 mL of methanol (99.5%, Sinopharm Chemical Reagent Co., Ltd.) were added to the mixture in an airtight Teflon-lined stainless steel autoclave. The autoclave was heated under stirring at 140°C for 24 h. The obtained solid was washed with water for several times and dried at 100°C overnight.

Desulphation of the samples was carried out as follows: the solid as-obtained above was added to a solution of 0.1 mol L^{-1} ammonium carbonate and stirred at 30°C for 2 h. The solid was filtered out and dried at 100°C overnight.

To prepare $\alpha\text{-PbO}$ for the electrochemical studies, the obtained desulphated solids were calcined at 450°C for 1 h in a muffle furnace.

The $\alpha\text{-PbO}$ samples prepared from the mixtures of lead sulphate and lead dioxide in mole ratios of 2:1, 1:1 and 1:2 were denoted as A, B and C sequentially in the context, while the one from spent batteries is called “the spent”.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were measured on a Bruker D8 Discover instrument operating at 40 kV and 20 mA, by using $\text{CuK}\alpha$ radiation ($\lambda = 0.15406\text{ nm}$), and their phase compositions were determined by the software Jade. Scanning electron micrographs (SEM) of samples were performed on a Hitachi S-4800 microscope.

2.3. Plate preparation

1.0 g of the as-prepared sample (A, B, C or the spent) was placed into a container, and then 0.003 g of fibres, 0.003 g of graphite, 0.124 mL of water and 0.11 mL of H_2SO_4 (36 wt.%) were added to it slowly. The amount of water added could be slightly modified to obtain the required density (4.0 g mL^{-1}). The plates were obtained by applying the paste evenly onto a $\text{Pb}\text{--}\text{Ca}$ alloy grid with dimensions of $10 \times 8 \times 2\text{ mm}^3$.

The plates were immersed in sulphuric acid of 8 wt.% for 5 s, and then put into an oven maintained at 100°C for 5 min, then put in a water bath, lowering the temperature to 75°C with relative humidity $>95\%$. The curing was conducted for 24 h. After that, the plates were dried at 70°C for 48 h. The mass of the active material is the mass difference of the dried plate subtracts the blank grid.

2.4. Electrochemical performance test

All the formation and the cycling tests were performed on an NEWARE Cycler (BTS-5V3A Shenzhen NEWARE Electronics Co., Ltd., China). The positive plate was assembled with a commercial negative plate (from commercial batteries, the area is about 3 times than the positive plate) and separated by absorptive glass-mat (AGM). The plates were assembled into a case and the electrolyte was H_2SO_4 solution with a relative density of 1.23 g mL^{-1} .

After the plate had been soaked for 2 h, the battery formation was started. The formation was divided into 3 steps. Firstly, the plate was charged at a current density of 15 mA cm^{-2} to 100 mAh g^{-1} ; then it is charged at 25 mA cm^{-2} for another 150 mAh g^{-1} ; and finally, it was charged at 8 mA cm^{-2} for another 100 mAh g^{-1} . Since the negative plate had a much larger capacity than the positive plate, the cell capacity was restricted by the positive plate.

After formation, the cell was discharged at 5 mA g^{-1} until the voltage fell to 1.75 V. Then it was used for cyclic tests. The plate was

firstly charged at 50 mA g^{-1} until the cell voltage reached to 2.45 V, then it was charged at 25 mA g^{-1} until the charged charges was 110% of the first discharge capacity after formation. The plate was then discharged at a current density of 50 mA g^{-1} . This was done for 50 cycles.

The cyclic voltammetry (CV) was carried out on a CorrTest model CS350 electrochemical working station (WUHAN CORRTTEST Instrument Co., Ltd., China). The CV curves were determined with a typical three-electrode system. The working electrode was prepared with a plate filled with lead monoxide, and a double platinum electrode was used as the counter electrode while the $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (sat.) was employed as the reference electrode. Sulphuric acid (36 wt.%) was used as the electrolyte. The measurement was carried out at a potential scan rate of 20 mV s^{-1} from 0 to 1.8 V.

3. Results and discussion

3.1. Treatments of the mixtures of PbSO_4 and PbO_2

Fig. 1 shows the schematic flow sheet of the treatments of the mixtures. The treatments were divided into three steps: solvothermal reduction, desulphation and calcination. Compare to our previous report [19], the present procedure is different only in the sequence of solvothermal reaction and desulphation (or carbonation). We did the solvothermal treatment first to find out if lead sulphate has any effect on the solvothermal reaction as well as the electrochemical property of the final product.

3.2. The solvothermal reaction of mixtures in methanol

We have reported that solvothermal treatment of PbO_2 in methanol reduces PbO_2 to PbO or $\text{PbO} \cdot \text{PbCO}_3$ at 140°C for 24 h [18]. Therefore, the solvothermal reactions of the mixtures are performed again under the same conditions. The XRD patterns of the solids after solvothermal reaction are shown in Fig. 2, which shows that they are mainly composed of PbSO_4 and $\text{PbO} \cdot \text{PbSO}_4$, but a small amount of $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$ can be identified at least in sample c. It can be observed that the peaks of $\text{PbO} \cdot \text{PbSO}_4$ are strongest in all the three samples, and those of PbSO_4 are higher when content of lead sulphate is higher in the original mixture. Only very small amount of PbSO_4 can be identified in sample c. The reason is that the raw mixture of sample c contains PbSO_4 and PbO_2 in a molar

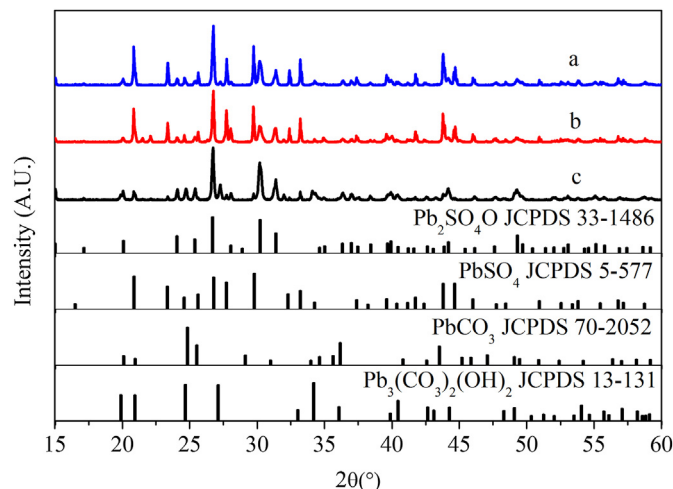
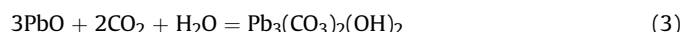


Fig. 2. XRD patterns of the samples after solvothermal reaction. The molar ratios of lead sulphate and lead dioxide in samples were 2:1 (a), 1:1 (b) and 1:2 (c).

ratio of 1:2, there is not enough PbSO_4 for the Reaction (2), therefore, Reaction (3) takes place instead:



Compared with our previous report [19], in which carbonated mixture of PbO_2 and PbSO_4 (that is, a mixture of PbO_2 and PbCO_3) is reacted with methanol, the main difference is that $\text{PbO} \cdot \text{PbSO}_4$ forms here instead of $\text{PbO} \cdot \text{PbCO}_3$. In both cases, either PbCO_3 or PbSO_4 is reactive and can react with PbO produced in the methanol reduction to form a basic salt. It can be deduced that as-formed PbO should be coated on the surface of PbSO_4 (or PbCO_3) originally coexisted in the reaction mixture, and they then react to form $\text{PbO} \cdot \text{PbSO}_4$ (or $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$).

We are then interested in finding out if the surface reactions can affect the morphology of the basic salt. Fig. 3 shows the SEM micrographs of the PbO_2 , PbSO_4 and the mixtures after solvothermal reduction. The SEM micrographs of PbO_2 (Fig. 3A and B) show that PbO_2 particles used in the experiments are very irregular in shape and size (Fig. 3A), and the big particles are aggregates of much smaller particles (Fig. 3B). The PbSO_4 particles (Fig. 3C) are roundish but generally a bit long in one dimension, and their sizes distributed in several micrometres. However, the particles of methanol thermal products are all rod-like (Fig. 3D–F), and the diameter of the rods is around $0.5 \mu\text{m}$, but the length could be several micrometres. Compared to their parent particle of PbSO_4 , they are much smaller, but they may inherit the morphology of PbSO_4 in that they prefer to grow in a dimension. As we have pointed out in above context, the PbO formed in the reduction must coat on the particles of PbSO_4 , and then react with the latter. It is known that the reactivity of different lattice face is different; consequently, the crystal habit of PbSO_4 will affect the growth of the crystal of the basic salt, which results in the inheritance. Because the diffusion of the ions on a crystal surface, which are needed for the growth of the product crystals, is difficult, the crystals of product are difficult to be big [24,25].

3.3. Desulphation of the samples

The XRD patterns of the samples after desulphation are shown in Fig. 4, which show that the solids are only PbCO_3 . Therefore, both

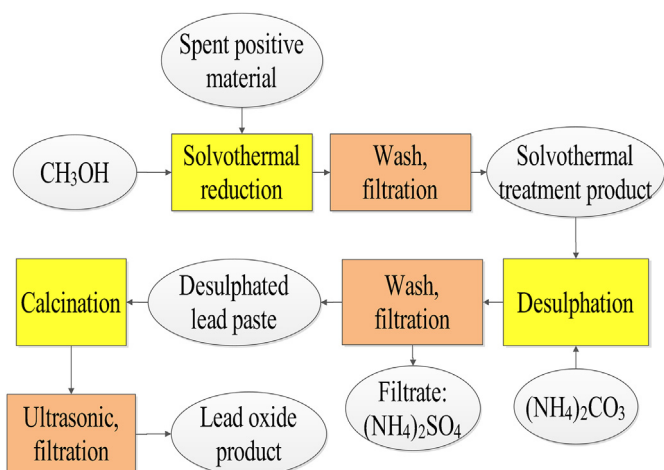


Fig. 1. Schematic flow sheet of the novel process for spent positive materials.

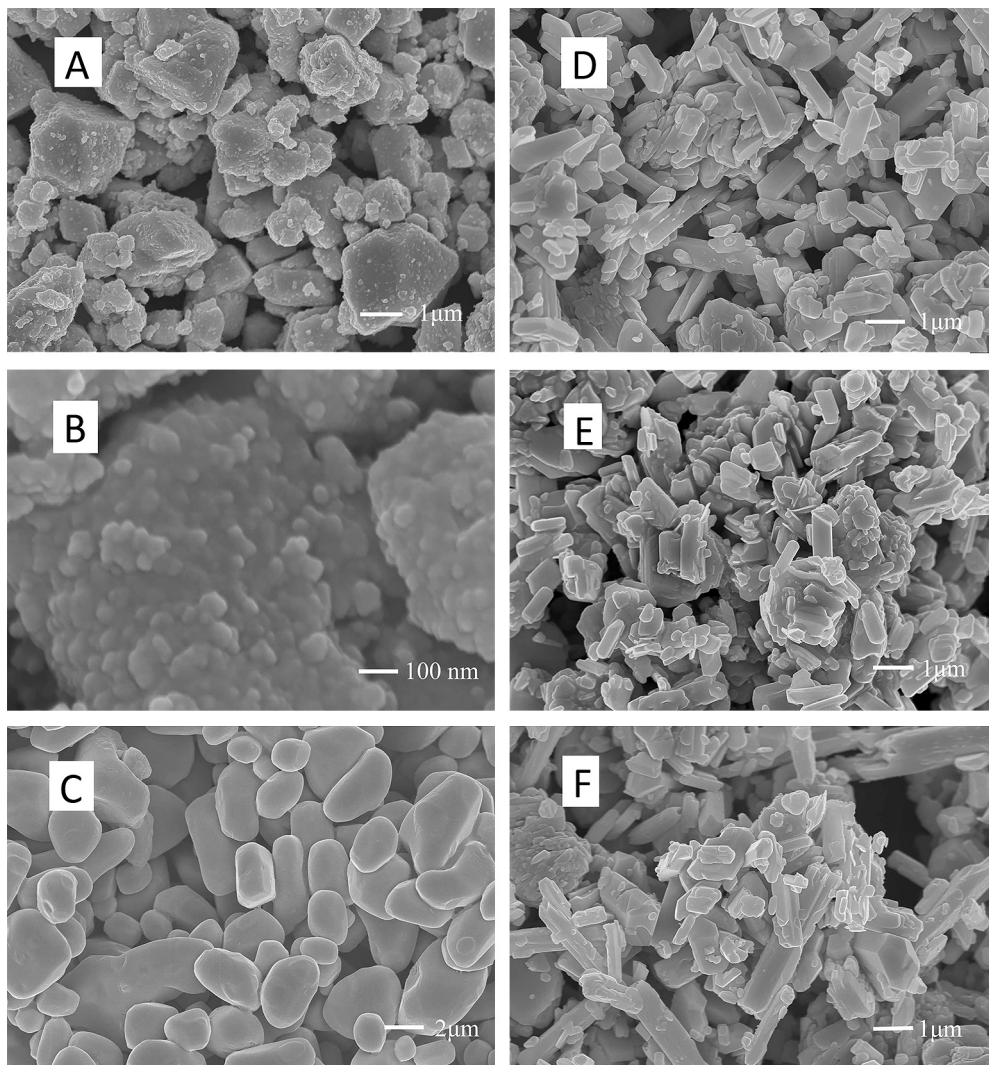


Fig. 3. SEM micrographs of the (A, B) PbO_2 , (C) PbSO_4 and (D, E, F) samples obtained after solvothermal reaction. The mole ratios of lead sulphate and lead dioxide in the raw materials were (D) 2:1, (E) 1:1 and (F) 1:2.

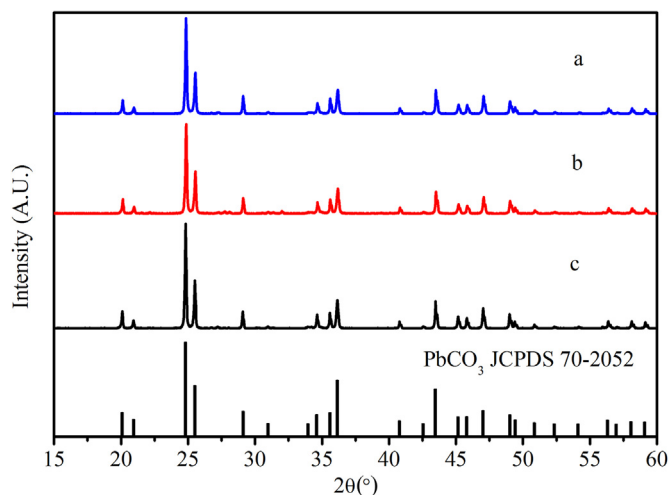


Fig. 4. XRD patterns of the samples after desulphation. The mole ratios of lead sulphate and lead dioxide in samples were 2:1 (a), 1:1 (b) and 1:2 (c).

PbSO_4 and $\text{PbO} \cdot \text{PbSO}_4$ are easily reacted with $(\text{NH}_4)_2\text{CO}_3$ to form PbCO_3 , which is the same as observed previously [19]. The involved reactions are as follows:

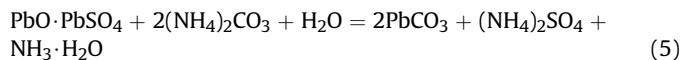
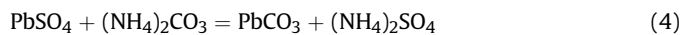


Fig. 5 shows the SEM micrographs of the samples obtained after the desulphation. To compare with what happens if sole PbSO_4 is used, the XRD patterns and SEM micrographs of carbonated PbSO_4 are also presented in Fig. 5A–C. It is obvious that the carbonated (or desulphated) PbSO_4 is only PbCO_3 , which indicates that PbSO_4 is completely converted during the desulphation; and its particles are irregular chained-smaller particles of PbCO_3 , sized about 400 nm, which aggregate to grains sized about several micrometres. Compared with Fig. 3C, the particles of PbSO_4 are similar in size to the secondary grains, which may mean that PbCO_3 forms from the gradual etching of CO_3^{2-} and direct deposition on the surface of PbSO_4 particle. As we have pointed out before, it can be understood that the particles of PbCO_3 are much smaller than those of PbSO_4 ,

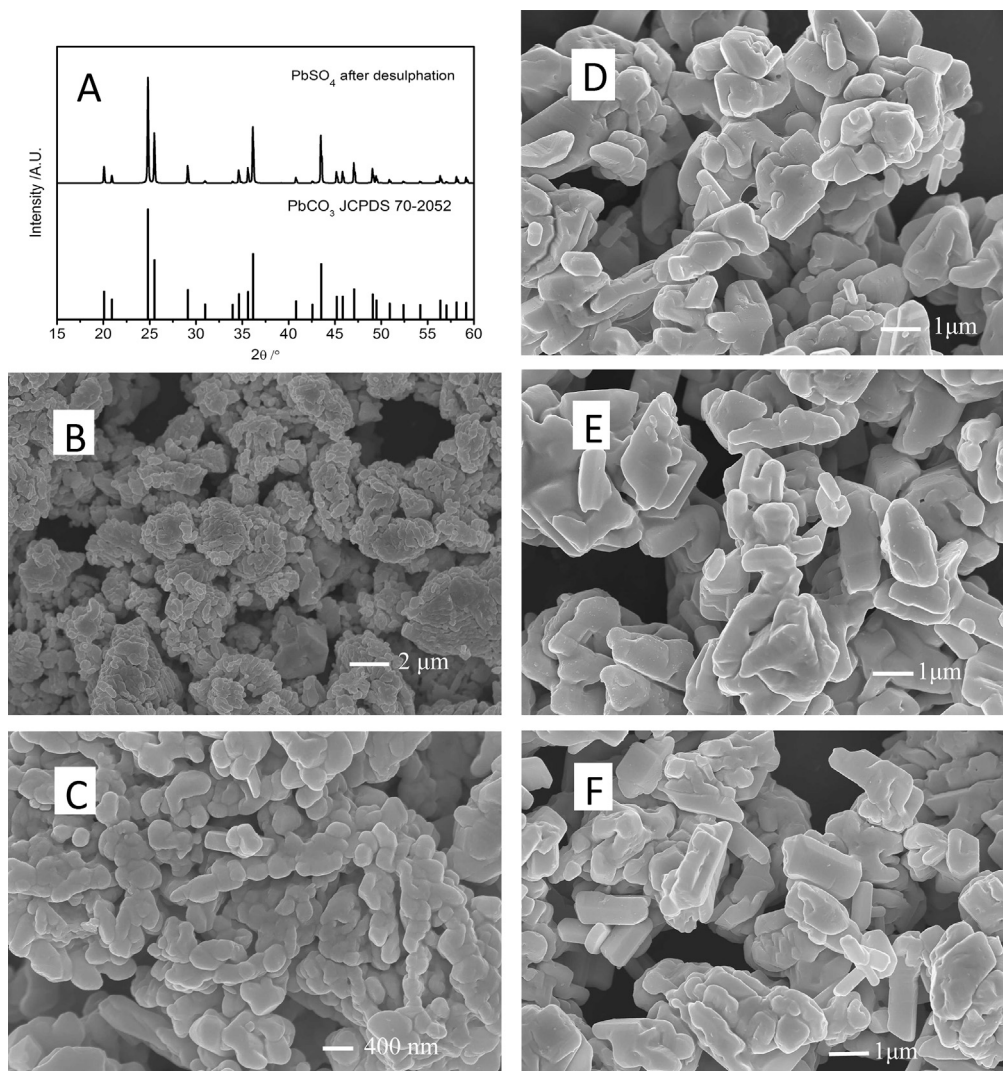


Fig. 5. XRD pattern and SEM micrographs of the PbSO_4 and the mixture samples after desulphation reaction. (A) XRD pattern and (B, C) SEM micrographs of PbSO_4 after desulphation. The mole ratios of lead sulphate and lead dioxide in samples were (D) 2:1, (E) 1:1 and (F) 1:2.

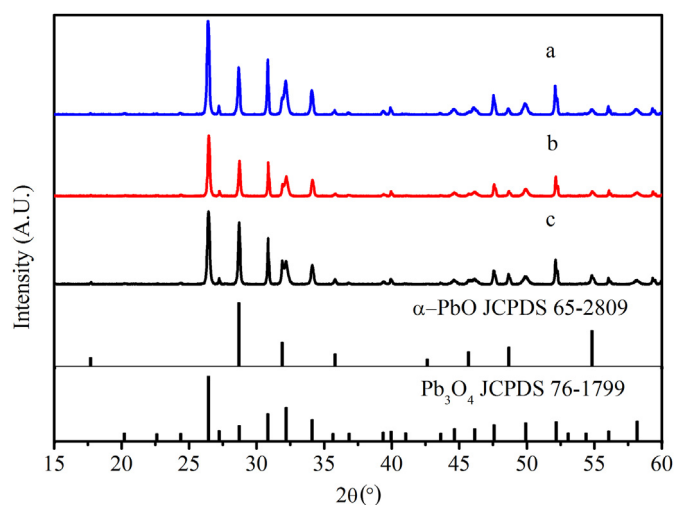


Fig. 6. XRD patterns of the samples after calcination. The mole ratios of lead sulphate and lead dioxide in samples were 2:1 (a), 1:1 (b) and 1:2 (c).

because diffusion in solids is always difficult, which limited the growth of the crystalline of product [24,25]. In addition, the chained particles of PbCO_3 may come from the different reactivity of crystallographic plane, which makes the chains parallel to each other in one grain (Fig. 5B and C).

The morphologies of the desulphated mixture of $\text{PbO} \cdot \text{PbSO}_4$ and PbSO_4 , which are obtained from the methanothermal treatment of mixtures of PbO_2 and PbSO_4 , show similarities to their parent mixture (Fig. 5D–F and Fig. 3D–F). There are many rod-like particles with diameter of 1 μm , which aggregate to bigger particles. Compared with their parent particles, they are a little bit bigger, and all the three samples are similar in morphology. Consequently, morphology inheritance exists more or less here. This can also be understood from the different reactivity of crystallographic plane as above.

3.4. The calcination of solid samples after desulphation

Fig. 6 gives the XRD patterns of calcined PbCO_3 prepared from desulphation previously, which shows that there are only α - PbO and Pb_3O_4 in the products (Fig. 6a–c). According to the XRD patterns, the compositions were determined with the software

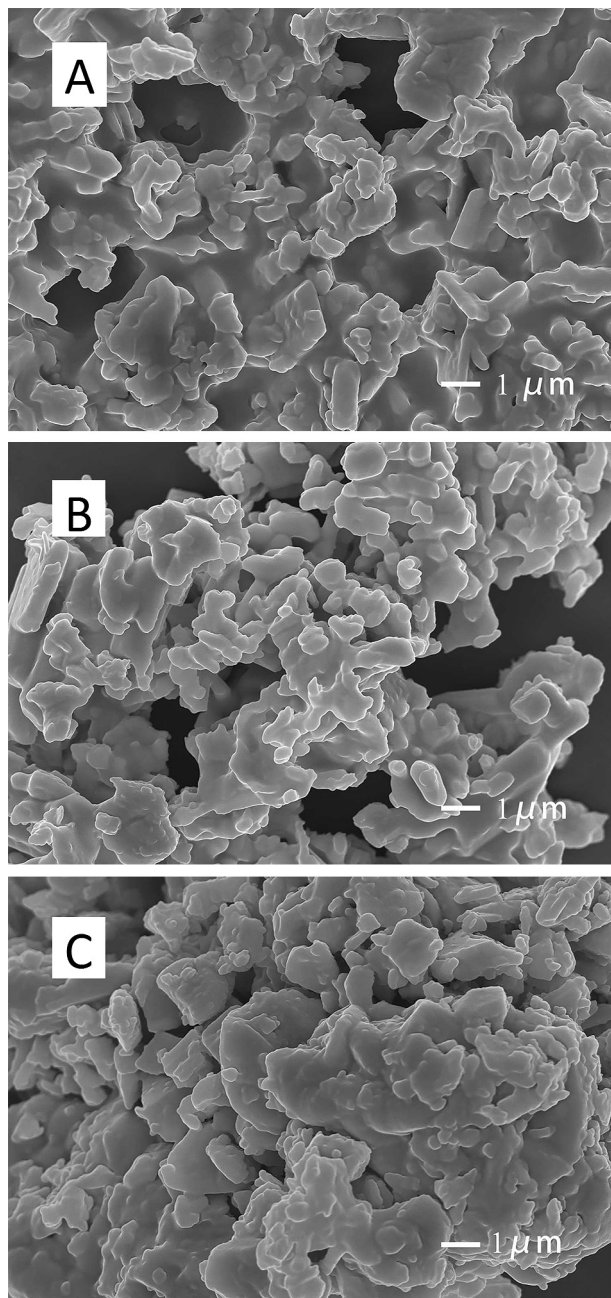


Fig. 7. SEM micrographs of the solid samples after calcination at 450 °C for 1 h. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

Jade, which are listed in Table 1. The weight percentage of Pb_3O_4 in the mixtures is between 20.7 and 24.2%, which are a little smaller than pre-desulphation method in our previous (about 26.6%) [19].

Fig. 7 shows the SEM micrographs of the three calcined samples. It shows that all the three samples are seriously aggregated particles with a size distribution ranging from 0.5 to 3 μm . Comparing to our previous reports, all the particles there are not so aggregated, and the particles from PbO_2 are rod-like with a diameter of around 500 nm and length of several micrometre [18], the particles from the mixtures of PbO_2 and PbSO_4 are irregular, especially for the two mixtures with higher content of PbSO_4 [19]. The particle size of the current products is also a little bigger.

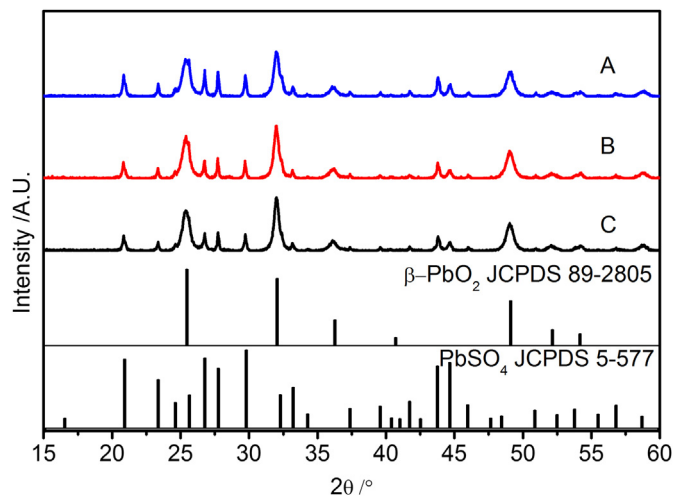


Fig. 8. XRD patterns of the samples after formation. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

3.5. The formation of the samples in the positive plate of a lead acid battery

The XRD patterns of the three samples after formation are shown in Fig. 8. It displays that all the three samples are similar and contain mainly $\beta\text{-PbO}_2$ and small amount of PbSO_4 . By using the software Jade, the contents of PbO_2 are calculated and given in Table 2. Combined with Table 1 and Fig. 6, it could be concluded that higher amount of existence of Pb_3O_4 may enhance the formation. This is in accordance with the general knowledge on this particulate issue [26–28]. Compare to pre-desulphation method [19], the contents of $\beta\text{-PbO}_2$ in the three samples are also lower, which should be related to their lower contents of Pb_3O_4 in the three as-prepared samples.

To observe the morphology changes of the sample after formation, the active materials were peeled from the plate after formation, and then grinded for SEM observations. It can be seen from Fig. 9 that the particles are rod-like and much smaller after formation. This is very similar to those in our previous reports [18,19].

3.6. Electrochemical performance of the prepared samples

Cyclic performance under a discharge current density of 50 mA g^{-1} of the three samples are shown in Fig. 10. It displays that the capacity of all the three samples is quite stable within 50 cycles, and their discharge capacities are all about 120 mAh g^{-1} . In comparison with the electrochemical performance of the product obtained from methanothermally reduced PbO_2 in methanol, the results show that, the discharge capacities of the products are as good as it. But comparing with our previous report on pre-desulphation [19], where the discharge capacities are above 120 mAh g^{-1} , the current samples may behave similarly. We have noticed that there are less content of $\beta\text{-PbO}_2$ in the current samples than the formers, which leads to less the content of $\beta\text{-PbO}_2$. It has been found that the content of $\beta\text{-PbO}_2$ determines the performance of the plate [29,30], we believe that the presence of PbSO_4 in the raw mixtures has little to do with the electrochemical performance of the products, also, the pre- or post-desulphation has little effect on the performance of the final product.

To obtain the rate performance of the as-prepared samples, their discharge capacities are measured and plotted versus discharge current densities in Fig. 11. As expected, the discharge capacity

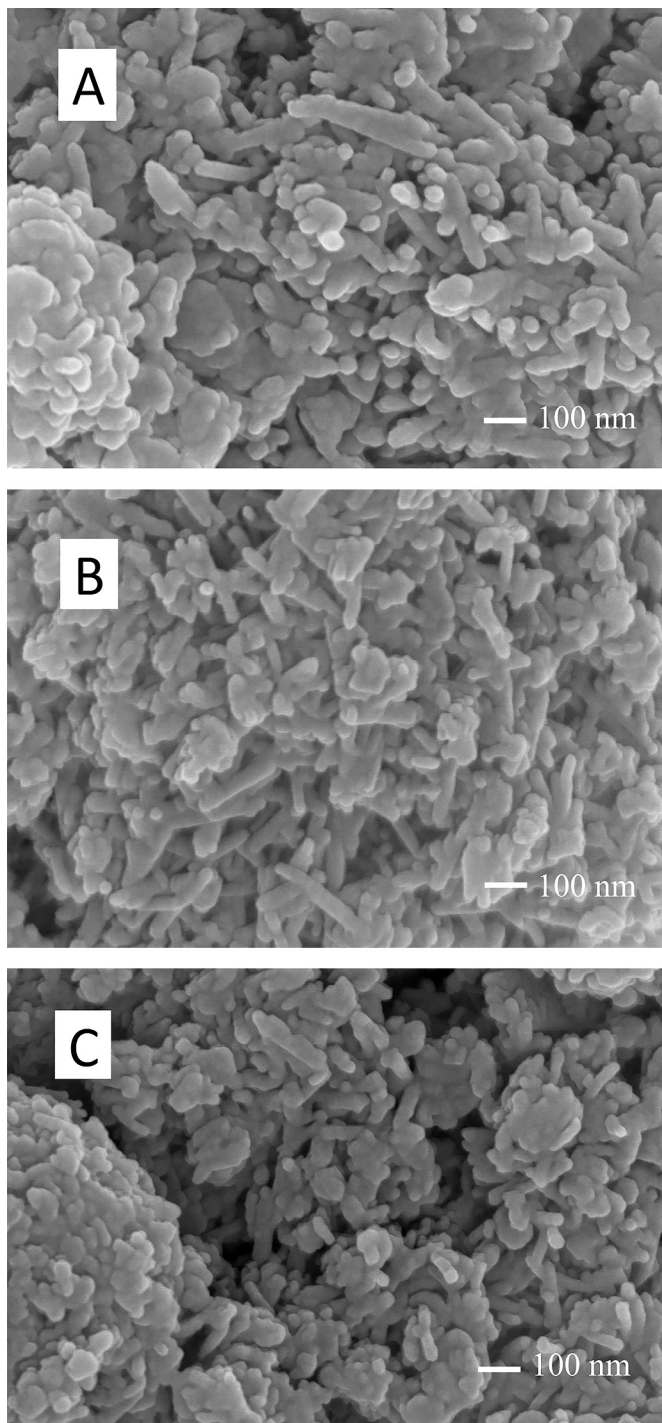


Fig. 9. SEM micrographs of the samples after formation. The mole ratios of lead sulphate and lead dioxide in samples were (A) 2:1, (B) 1:1 and (C) 1:2.

decreases as the current density increases. All the three samples behave very similarly, which discharge about 165 mAh g^{-1} at 5 mA g^{-1} , 80 mAh g^{-1} at 200 mA g^{-1} and 60 mAh g^{-1} at 400 mA g^{-1} . If the utilization of active material is defined as the ratio of the discharged capacity to the corresponding theoretical capacity, and the theoretical capacity of pure PbO is 240 mAh g^{-1} , Those of the three samples are about 68% at the discharge current density of 5 mA g^{-1} . This is about the same as the pre-desulphation method.

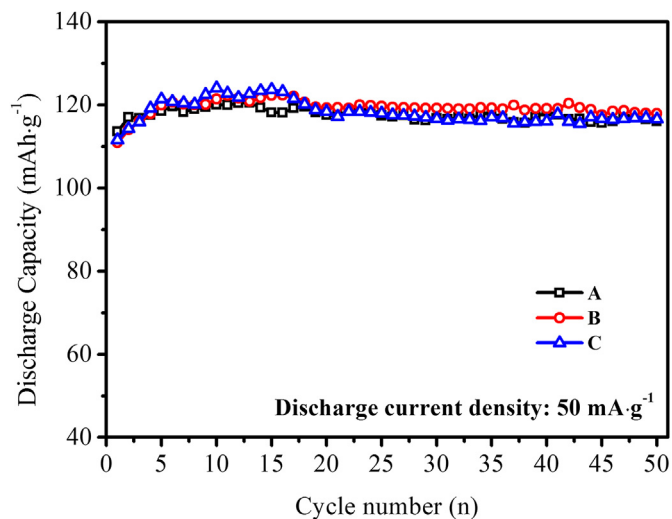


Fig. 10. The discharge capacities of the three samples versus cycle number.

The as-prepared samples have also been examined by cyclic voltammetry after the 50th cycle (Fig. 12), which show similar results to that of Visser [31]. The oxidation of PbSO_4 to PbO_2 occurs at 1.25 V (versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ in sat. K_2SO_4), the evolution of oxygen occurs beyond 1.4 V, and the reduction of PbO_2 to PbSO_4 occurs at 0.85 V. All the CV curves are similar, and cathode current is much higher than the anode current.

3.7. The treatments and the electrochemical performance of the positive material from spent lead acid battery

Fig. 13 compares the SEM micrographs of the samples obtained after the calcination and formation for both pre-desulphation method and post-desulphation method. It can be seen that the samples prepared by two methods are basically similar in size and morphology. The particle sizes become much smaller after formation as afore-mentioned.

Fig. 14 shows electrochemical performance of the sample obtained from the spent positive material after the same treatments as that for the mechanical mixtures. Cyclic performance of the spent sample is shown in Fig. 11A, which shows that the capacity is around 120 mAh g^{-1} within 50 cycles. Its capacity loss is about 5%

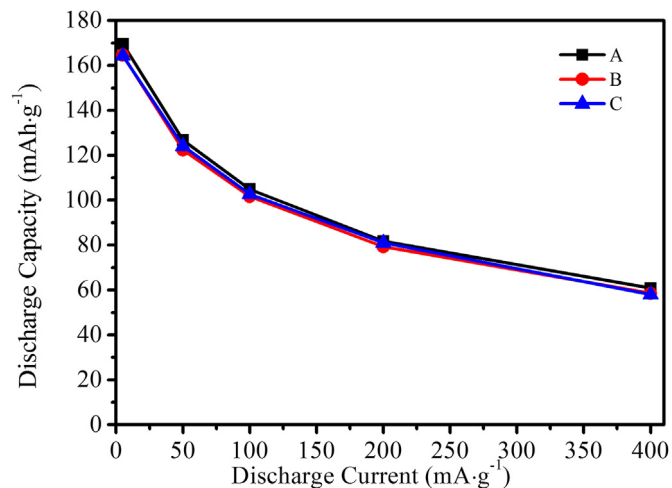


Fig. 11. Discharge capacity versus the current density of the three samples.

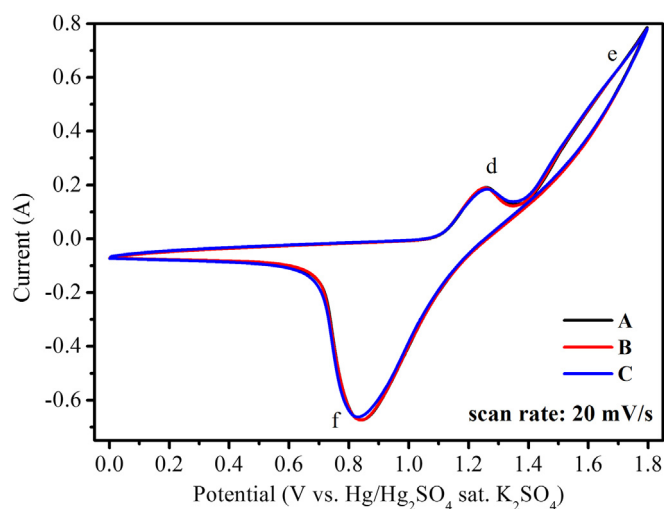


Fig. 12. Cyclic voltammetry curves of the three samples.

within 50 cycles under 100% DOD. Fig. 14b shows the curve of discharge capacity versus the discharge current density. The discharge capacities are about 170 mAh g^{-1} at the current density of 5 mA g^{-1} , and 60 mAh g^{-1} at 400 mA g^{-1} . The material utilization is about 70%.

Table 3 lists the discharge capacities of all the related samples at different current densities. Generally, all these samples behave similarly and slightly depending on the raw material; but as the discharge current density increases, the deviation to the average increases and the maximum deviation appears for the capacity loss of the spent samples after 50 cycles. Generally, samples prepared according to the post-desulphation method are better than the pre-desulphation method. Those results tell that the product of the methanothermal reduction of PbO_2 -containing mixture may change, depending definitely on the composition of the starting

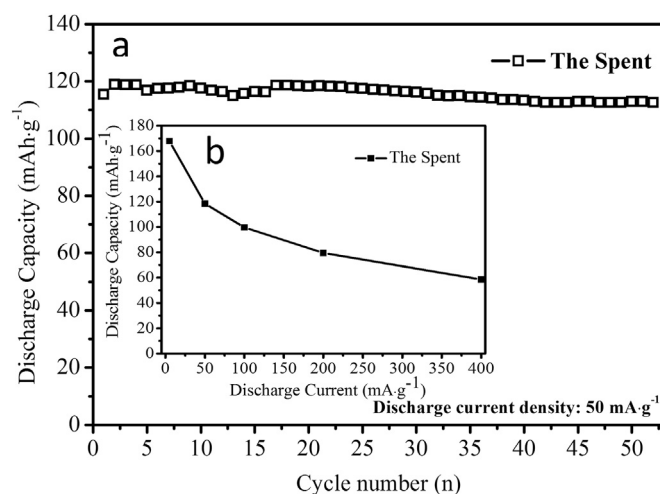


Fig. 14. Electrochemical performance of the positive material from spent lead acid battery after treatments.

mixture, but the final PbO and its property are hardly dependent on the composition. We believe that it is because the product of reduction is calcined, and the calcination makes the completely change both in chemical composition and structure; there is little influence on the structure, morphology and size of PbO the final product, consequently little influence on the property.

4. Conclusion

This paper investigates methanothermal reduction of mixtures of PbO_2 and PbSO_4 , which are obtained from both mechanical mixing of the components and the active materials of positive plates of spent lead acid batteries, and subsequent chemical treatments to obtain PbO for new lead acid batteries. The results show that PbO_2 in each of the mixtures can be reduced by methanol

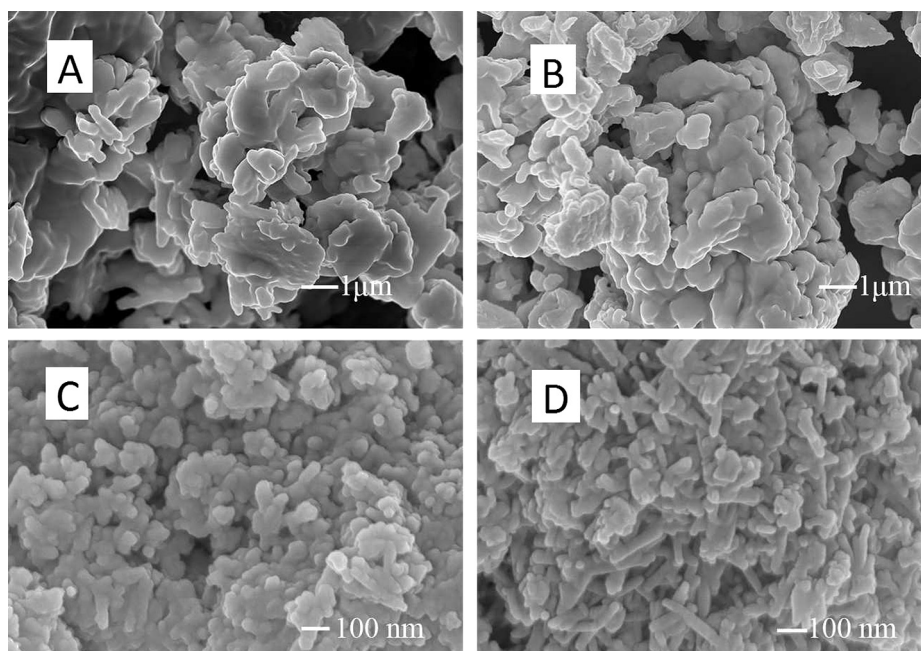


Fig. 13. The comparison of SEM micrographs of the samples from spent lead acid batteries for both the pre- and post-desulphated treatments. For the pre-desulphated samples: (A) sample after calcination and (C) the sample after formation; the post-desulphated sample: (B) sample after calcination and (D) the sample after formation.

Table 1

The composition of the samples A, B and C after calcination.

Sample	Composition (wt.%) ^a	
	α -PbO	Pb ₃ O ₄
A	76.7	23.3
B	75.8	24.2
C	79.3	20.7

^a The compositions were determined according to the XRD patterns shown in Fig. 4 with the software Jade.

Table 2The contents of PbO₂ after formation determined by the Jade software.

Sample	Contents of β -PbO ₂ (wt.%)
A	91.9
B	92.6
C	89.4

Table 3

The comparison of discharge capacities of all the as-prepared samples from different methods or start materials.

Samples ^a	Discharge capacity (mAh g ⁻¹) at different current density					Capacity loss after 50th cycle
	5 mA g ⁻¹	50 mA g ⁻¹	100 mA g ⁻¹	200 mA g ⁻¹	400 mA g ⁻¹	
Pure PbSO ₄ [23]	—	120.0	—	—	—	8.0%
Pure PbO ₂ [18]	167.4	120.1	112.5	91.5	—	3.3%
Pre-A [19]	170.7	125.4	103.0	80.5	61.9	6.0%
Pre-B [19]	169.4	132.0	108.1	86.0	65.0	6.1%
Pre-C [19]	164.6	125.1	101.8	81.6	62.6	5.4%
Pre-spent [19]	162.1	127.0	97.5	78.4	40.0	9.8%
Post-A	169.6	126.8	104.9	81.8	60.9	3.7%
Post-B	164.6	122.4	101.6	79.3	58.5	3.5%
Post-C	164.4	124.1	102.7	81.0	58.0	4.5%
Post-spent	168.9	118.6	99.7	79.5	59.5	5.0%
Average	166.8	124.2	103.5	82.2	58.3	5.5%

^a Pre- and post- are short for pre-desulphation method and post-desulphation method. The mole ratios of lead sulphate and lead dioxide in samples are (A) 2:1, (B) 1:1 and (C) 1:2. The spent is the sample from spent positive material.

at 140 °C in 24 h, which produces PbO, and the PbO reacts subsequently with the coexisted PbSO₄ to produce PbO·PbSO₄. That mixture can be easily desulphated with (NH₄)₂CO₃ to form PbCO₃, and the PbCO₃ can be baked in air to form a mixture of α -PbO and Pb₃O₄ at 450 °C for 1 h.

SEM observations show that the as-prepared PbO·PbSO₄ may inherit and enhance the morphological characteristics of PbSO₄, which is somewhat rod-like. In addition, carbonation of PbO·PbSO₄ does not destroy the rod-like characteristics.

Electrochemical performances of the three samples reveal very similar discharge capacities, which are about 165 mAh g⁻¹ at 5 mA g⁻¹, and 60 mAh g⁻¹ at 400 mA g⁻¹; they also have nice cyclic stability in 50 cycles.

The same treatments have been done to the sample from spent positive active material. The results show that the capacity is

around 120 mAh g⁻¹, and its capacity loss is about 5% in 50 cycles. In addition, the reused sample gives a good discharge capacity at high discharge rate than that in pre-desulphation method. That may be because of the existence of PbSO₄ in solvothermal reaction. We will do more researches to figure out the mechanism.

Compared with our previous reports on pure PbSO₄, PbO₂ and the same mixture treated with pre-desulphation method, the discharge capacities are similar under the same condition, but the discharge capacities are more stable for the samples prepared according to the post-desulphation method.

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